Olefin Cross-Metathesis with Vinyl Halides

Volodymyr Sashuk, Cezary Samojłowicz, Anna Szadkowska, Karol Grela* Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland RECEIVED DATE (automatically inserted by publisher); E-mail grela@icho.edu.pl

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1. General

1.1. Equipment and chemicals used

All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The anhydrous solvents were dried by distillation over CaH₂ and were transferred under argon: (*E*)-1,2-dichloroethene (Fluka), (*Z*)-1,2-dichloroethene (Aldrich, contains 15% mol of *E* isomer), CH₂Cl₂.

Flash column and preparative thin layer chromatographies were performed using silica gel 60 (230–400 mesh). NMR spectra were recorded in CDCl₃; chemical shifts (δ) are given in ppm relative to TMS, coupling constants are (J) in Hz. IR spectra: wavenumbers are in cm⁻¹. MS (EI, LSIMS) spectra were recorded on AMD 604 Intectra GmbH spectrometer. MS (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc. GC/MS measurements were done on HP 5890 with HP 5 column.

Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw.

Catalysts **1a** and **1b** were purchased from Aldrich and used as received. Complexes $\mathbf{1c}^{1}$ and $\mathbf{1d}^{2}$ were prepared according to literature methods. All other commercially available chemicals were used as received.

1.2. Analytical methods

Comparative CM experiments with diene 5a (refer to Scheme 1): To a stirred solution of diene 5a (0.2 mmol, 26.8 mg) and durene (used as an internal standard, 0.1 mmol) in (*E*)-1,2-dichloroethene (100 equiv., 1.6 mL) placed under argon in a Schlenk tube a catalyst (0.001–0.005 mmol) was added in a single portion at room temperature and the reaction mixture was refluxed for 20 h. Reaction mixtures were immediately analysed by GC, using HP 6890 chromatograph with HP 5 column. The responses of the FID detector were calibrated using 5a/durene and 7a/durene standard solutions. Each CM experiment was repeated at least two times.

¹ (a) K. Grela, S. Harutyunyan; A. Michrowska, *Angew. Chem. Int. Ed.*, 2002, **41**, 4038; (b) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, *J. Am. Chem. Soc.*, 2004, **126**, 9318.

² M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Arlt, K. Grela, J. Am. Chem. Soc., 2006, 128, 13652.

2. Experimental section

2.1. General procedure for CM reactions

To a solution of alkene (0.60 mmol) in (*E*)-1,2-dichloroethene (100 equiv., 4.6 mL) was added a Ru-catalyst as a solid by portions (one portion per hour) or in one portion (0.03–0.09 mmol, 5.0–15.0 mol%). The resulting mixture was refluxed for 6–24 h. The solvent was removed under reduced pressure. The crude product was purified by flash or preparative thin layer chromatography (*c*-hexane/EtOAc).

2.2. Characterisation data

1-[(*E*,*Z*)-2-Chloroethenyl]-4-methoxybenzene (7a)

The crude product was purified by preparative thin layer chromatography (*c*-hexane/EtOAc = 20:1). Colorless oil (91%). Mixture of isomers, Z:E = 5:1.

IR (film) v 3079, 3005, 2957, 2837, 1606, 1574, 1510, 1462, 1345, 1304, 1257, 1174, 1033, 833, 787, 691, 536 cm⁻¹;

¹**H** NMR (400 MHz, CDCl₃) δ 7.68 – 7.64 (m, 2H), 7.25 – 7.21 (m, 2H), 6.93 – 6.89 (m, 2H), 6.88 – 6.84 (m, 2H), 6.78 (d, J = 13.7 Hz, 1H), 6.57 (d, J = 8.1 Hz, 1H), 6.51 (d, J = 13.7 Hz, 1H), 6.16 (d, J = 8.1 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H);

¹³**C NMR** (100 MHz, CDCl₃) δ 159.5 (s), 159.3 (s), 132.7 (s), 130.7 (s), 128.6 (s), 127.6 (s), 127.3 (s), 126.9 (s), 116.4 (s), 115.4 (s), 114.2 (s), 113.6 (s), 55.2 (s);

MS (EI) *m*/*z* (rel intensity): 168 (M^{+•}, 100), 153 (56), 125 (40), 89 (33), 63 (21);

HRMS (EI) calcd for C₉H₉O³⁵Cl 168.0342, found 168.0347;

EA Anal. calcd for C₉H₉OCl: C 64.11, H 5.38, Cl 21.02; found C 64.25, H 5.39, Cl 20.84.

(1-*E*,*Z*)-10-Bromo-1-chloro-1-decene (7b)

The crude product was purified by flash chromatography (pentane). Colorless oil (87%). Mixture of isomers, Z:E = 1.4:1.0.

IR (film) v 2928, 2856, 1630, 1464, 1439, 1347, 1246, 935, 802, 710, 646, 563 cm⁻¹;

¹**H NMR** (500 MHz, CDCl₃) δ 6.06 - 5.98 (m, 1H), 5.95 - 5.85 (m, 2H), 5.74 (q, *J* = 7.1 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 4H), 2.25 - 2.19 (m, 2H), 2.07 - 2.02 (m, 2H), 1.89 - 1.81 (m, 4H), 1.47 - 1.25 (m, 20H);

¹³C NMR (125 MHz, CDCl₃) δ 134.0 (s), 131.8 (s), 117.9 (s), 116.7 (s), 33.9 (s), 33.9 (s), 32.8 (s), 32.8 (s), 30.8 (s), 29.2 (s), 29.0 (s), 28.8 (s), 28.8 (s), 28.7 (s), 28.3 (s), 28.1 (s), 26.9 (s);

MS (EI) *m/z* (rel intensity): 254 (M^{+•}, 2), 150 (34), 148 (35), 137 (26), 135 (12), 109 (10), 97 (22), 95 (47), 83 (34), 82 (33), 81 (51), 75 (22), 69 (100), 68 (20), 67 (34), 55 (94), 43 (20), 41 (46);

HRMS (EI) calcd for $C_{10}H_{18}^{-79}Br^{35}Cl 252.0280$, found 252.0275;

EA Anal. calcd for C₁₀H₁₈BrCl: C 47.36, H 7.15; found C 47.59, H 7.14.

tert-Butyl{[(5-*E*,*Z*)-6-chloro-5-hexenyl]oxy}dimethylsilane (7c)

The crude product was purified by preparative thin layer chromatography (*c*-hexane/EtOAc = 20:1). Colorless oil (76%). Mixture of isomers, Z:E = 1.5:1.0.

IR (film) v 2953, 2931, 2858, 1630, 1471, 1388, 1361, 1255, 1104, 1006, 937, 836, 775, 709 cm⁻¹;

¹**H** NMR (400 MHz, CDCl₃) δ 6.02 (dt, J = 7.0, 1.6 Hz, 1H), 5.97 – 5.85 (m, 2H), 5.75 (q, J = 7.0 Hz, 1H), 3.65 – 3.58 (m, 4H), 2.28 – 2.20 (m, 4H), 2.11 – 2.04 (m, 4H), 1.59 – 1.36 (m, 4H), 0.89 (s, 9H), 0.89 (s, 9H), 0.05 (s, 6H), 0.05 (s, 6H);

¹³**C NMR** (100 MHz, CDCl₃) δ 133.9 (s), 131.7 (s), 118.0 (s), 116.8 (s), 62.8 (s), 62.8 (s), 32.3 (s), 32.2 (s), 32.1 (s), 30.7 (s), 26.7 (s), 26.0 (s), 25.2 (s), 24.7 (s), 18.3 (s), -5.3 (s); **HRMS** (TOF) calcd for C₁₂H₂₆O³⁵Cl Si 249.1441, found 249.1436.

{[(Z)-2-Chloroethenyl]sulfanyl}benzene (7d)

The crude product was purified by preparative thin layer chromatography (c-hexane/EtOAc = 20:1). Colorless oil (85%).



IR (film) v 3075, 1585, 1563, 1479, 1439, 1290, 1024, 835, 742, 689, 667, 479 cm⁻¹; ¹**H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.27 (m, 5H), 6.60 (d, *J* = 6.4 Hz, 1H), 6.19 (d, *J* = 6.4 Hz, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 133.9 (s), 130.5 (s), 129.3 (s), 128.6 (s), 127.6 (s), 115.4 (s);

MS (EI) *m*/*z* (rel intensity): 170 (M^{+•}, 40), 135 (100), 109 (15), 91 (50);

HRMS (EI) calcd for C₈H₇S³⁵Cl 169.9957, found 169.9950;

EA Anal. calcd for C₈H₇SCl: C 56.30, H 4.13, S 18.79, Cl 20.77; found C 56.55, H 4.05, S 18.52, Cl 20.68.

({[(Z)-2-Chloroethenyl]sulfanyl}methyl)benzene (7e)

The crude product was purified by flash chromatography (*c*-hexane/EtOAc = 20:1). Colorless oil (35%).



IR (film) v 3501, 2939, 2863, 1469, 1461, 1405, 1320, 1215, 1188, 1160, 794, 656, 605 cm⁻¹;

¹**H** NMR (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 5H), 6.28 (d, J = 6.4 Hz, 1H), 6.03 (d, J = 6.4 Hz, 1H), 3.95 (s, 2H);

¹³C NMR (100 MHz, CDCl₃) δ 137.3 (s), 128.8 (s), 128.7 (s), 127.5 (s), 114.6 (s), 37.1 (s);

MS (EI) *m*/*z* (rel intensity): 184 (M^{+•}, 11), 91 (100), 65 (15);

HRMS (EI) calcd for $C_9H_9S^{35}Cl 184.0114$, found 184.0121.

1-[(Z)-2-Chloroethenyl]-2-pyrrolidinone (7f)

The crude product was purified by flash chromatography (*c*-hexane/EtOAc/Et₃N = 4.0:1.0:0.1). Colorless oil (32%).



IR (film) v 3418, 2961, 1945, 1712, 1646, 1387, 1334, 1260, 1030, 808, 719, 643 cm⁻¹;

¹**H NMR** (500 MHz, CDCl₃) δ 6.92 (d, J = 6.8 Hz, 1H), 5.40 (d, J = 6.8 Hz, 1H), 4.11 (t, J = 7.1 Hz, 2H); 2.42 (t, J = 8.2 Hz, 2H), 2.14 – 2.07 (m, 2H);

¹³C NMR (125 MHz, CDCl₃) δ 174.9 (s), 123.4 (s), 99.9 (s), 47.6 (s), 29.8 (s), 18.6 (s);
MS (EI) *m/z* (rel intensity): 145 (M^{+•}, 19), 110 (100), 90 (62);
HRMS (EI) calcd for C₆H₈S³⁵CINO 145.0294, found 145.0289.

(1-*E*,*Z*)-10-Bromo-1-bromo-1-decene (7h)

The crude product was purified by flash chromatography (pentane). Colorless oil (34%). Mixture of isomers, Z:E = 1.0:1.8.

IR (film) v 2928, 2855, 1621, 1463, 1437, 1271, 1245, 1136, 938, 702, 616 cm⁻¹;

¹**H** NMR (400 MHz, CDCl₃) δ 6.20 – 5.98 (m, 4H), 3.41 (t, J = 6.9 Hz, 4H), 2.22 – 2.16 (m, 2H), 2.07 – 2.00 (m, 2H), 1.89 – 1.81 (m, 4H), 1.47 – 1.25 (m, 20H);

¹³**C NMR** (100 MHz, CDCl₃) δ 138.2 (s), 134.9 (s), 107.6 (s), 104.1 (s), 46.9 (s), 34.0 (s), 34.0 (s), 32.9 (s), 32.8 (s), 29.6 (s), 29.2 (s), 29.1 (s), 29.0 (s), 28.8 (s), 28.6 (s), 28.5 (s), 28.1 (s), 28.0 (s);

MS (EI) *m/z* (rel intensity): 298 (M^{+•}, 2), 148 (29), 121 (14), 95 (35), 83 (44), 69 (100), 55 (99), 41 (68);

HRMS (EI) calcd for $C_{10}H_{18}^{79}Br_2 295.9776$, found 295.9782;

2-*H*-2-(*E*,*Z*)-Chloroperdeutero-1-phenylethene (7g)

The crude product was filtered by short pad of silica gel. Mixture of isomers, Z:E = 2.6:1.

¹**H NMR** (200 MHz, CDCl₃) δ 6.66 (t, J = 2.0 Hz, 1H), 6.28 (t, J = 1.2 Hz, 1H); **MS** (TOF EI) m/z (rel intensity): 144 (M^{+•}, 100), 109 (100), 81 (95);

3. Copies of ¹H and ¹³C spectra













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